Thermomigration of aluminum-rich liquid wires through silicon

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The thermomigration of aluminum-rich liquid wires in n-type silicon was studied as a function of migration direction, wire direction, wire shape, and wire sizes. Wires below 100 μ in diameter migrate stably in the ⟨100⟩ direction if the wires were aligned along ⟨011⟩ or ⟨0$\bar{1}$1⟩ directions. Wires below 500 μ in diameter migrate stably in the ⟨111⟩ direction for any wire direction lying in the (111) plane. The steplike p-n junctions produced behind the migrating wires have ideal characteristics; e.g., 650 V breakdown for 10-Ω cm Si. Arrays of lines and thus planar p-n junctions were made to depths of 1 cm in bulk silicon with separations between junctions as small as 50 μ.

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I. INTRODUCTION

Pfann[1] used the temperature gradient zone melting method to produce p-n junctions within the bulk of a semiconductor. In this method, either sheets[2] or wires[3] of a suitable metallic liquid are moved through a semiconductor crystal in a thermal gradient, leaving behind doped liquid-epitaxy material. In the last two decades, this process of temperature gradient zone melting has been applied to a variety of semiconductor.[4–16] However, problems involving, principally, the stability of the migrating zones have prevented the utilization of this technique in semiconductor processing.

Recently, we have demonstrated that droplets[17] and planar zones[18] are stable during migration if the dimensions of these zones are sufficiently small.

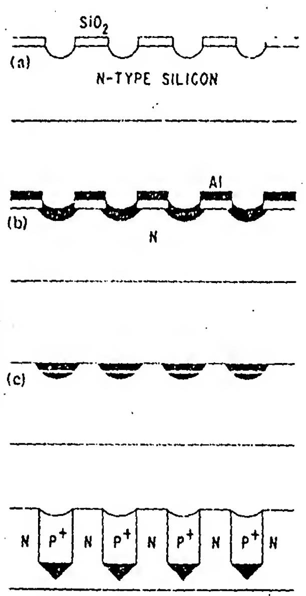


FIG. 1. The processing of a line array: (a) the wafer is oxidized, patterned and etched; (b) the aluminum is deposited on the etched face of the wafer; (c) excess aluminum is ground off; (d) the aluminum-rich liquid wires are migrated through the wafer with a thermal gradient.

Although a variety of semiconductor devices can be made with stable droplets and planar zones,[14,19–24] many applications require an array of planar p-n junctions which could be most easily obtained by migrating a stable array of liquid wires through a semiconductor crystal. Consequently, we have studied the thermomigration of aluminum-rich liquid wires through n-type silicon for a variety of wire sizes and crystallographic directions.[25] A number of stable wire directions, migration directions, and wire sizes were found. The planar step p-n junctions produced in these experiments have ideal characteristics (e.g., 650 V breakdown for 10-Ω-cm Si) which will be reported in a later paper on lamellar devices.

II. MIGRATION OF THE LIQUID WIRES

A. Experimental procedure

n-type 10 Ω cm single crystals (1 in. in diameter) of silicon with ⟨100⟩ and ⟨111⟩ axial orientations were obtained from Texas Instruments. Wafers 1 cm thick were sliced, polished, and oxidized. Line-array windows were etched through the overlaying oxide using photolithography techniques. With the oxide as a mask,

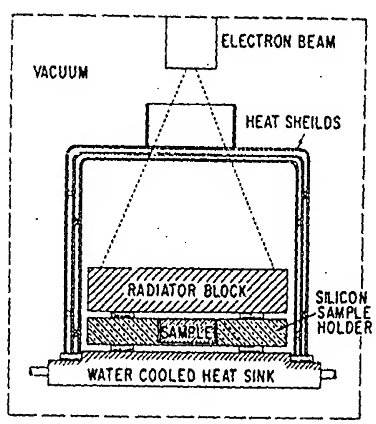


FIG. 2. The electron beam thermomigration apparatus used to produce thermal gradients in the silicon wafer. Heat flow from the radiator block to the sample and from the sample to the cooling is by radiation.

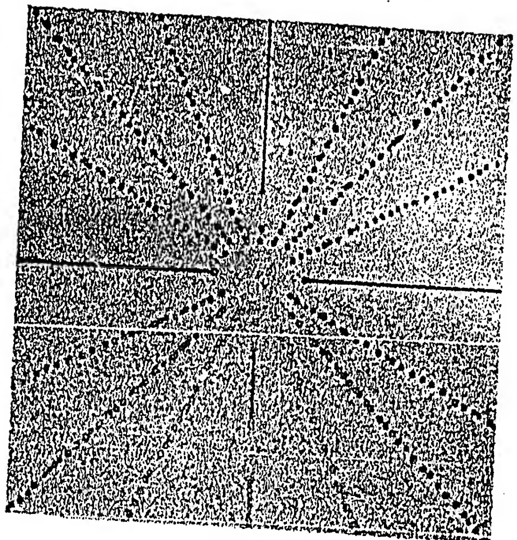


FIG. 3. A radial "sun" array of wires lying in the (100) plane after migration 3 mm down a ⟨100⟩ axis in silicon. Only wires lying along the ⟨011⟩ and ⟨01̄1̄⟩ directions are stable.

the line arrays were etched to a depth of 20 μ in the bulk silicon [Fig. 1(a)]. Then, a 20-μ-thick aluminum film was deposited from an electron beam source into the line array etched in the silicon [Fig. 1(b)]. The excess aluminum overlaying the oxide mask was ground off leaving etched line array grooves filled with aluminum to form the initial wires [Fig. 1(c)].[14] Finally, the sample was placed in the electron beam thermomigration apparatus shown in Fig. 2 which was designed to produce a very uniform vertical temperature gradient. In the experiments, a thermal gradient of 50 °C/cm at 1200 °C in a vacuum of 10^{-5} Torr drove the wires through a 1-cm wafer in less than 12 h.

After migration, the line-array pattern on the exit and entrance side of the wafer was revealed by polishing and chemical staining. In addition, the wafer was sectioned longitudinally to determine the shape of the trail left behind the migrating wire at various depths in the wafer.

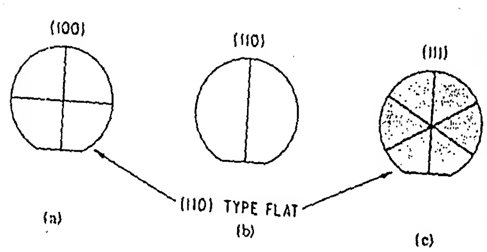


FIG. 4. The crystallographic direction of wires which can migrate stably in silicon in the (a) ⟨100⟩ direction, (b) ⟨110⟩ direction, and (c) ⟨111⟩ direction.

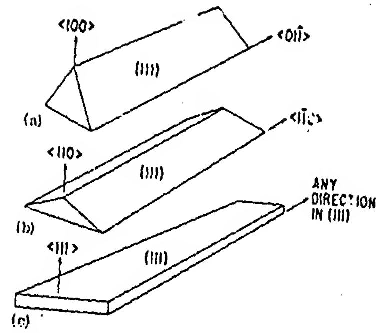


FIG. 5. The morphological shapes of wires which migrate stably in the (a) ⟨100⟩ direction, (b) ⟨110⟩ direction, and (c) ⟨111⟩ direction.

B. Experimental results

1. ⟨100⟩ axial wafers

A radial "sun" pattern of lines was used to determine the wire directions which migrate stably in the ⟨100⟩ direction. The resulting trail structure after migrating 3 mm into the silicon wafer is shown in Fig. 3. Only the wires lying in the vertical ⟨011⟩ and horizontal ⟨011̄⟩ directions are stable [Fig. 4(a)]. The shape of these stable wires is shown schematically in Fig. 5(a). Figure 3 shows that surface tension has caused coarsening at the ends of these stable wires.

Wires lying in the ⟨001⟩ and ⟨010⟩ directions (diagonally in Fig. 3) are unstable and break up into a row of pyramidal square-base droplets[15,16,22] because of severe faceting of the solid-liquid interface of wires lying in these directions. Wires lying in the ⟨012⟩ and ⟨021⟩ directions are also unstable (Fig. 3). Figure 4(a) summarizes the crystallographic directions of lines which can migrate stably in the ⟨100⟩ direction.

In addition to the crystallographic direction of wires, their size also influences their stability. Figure 6

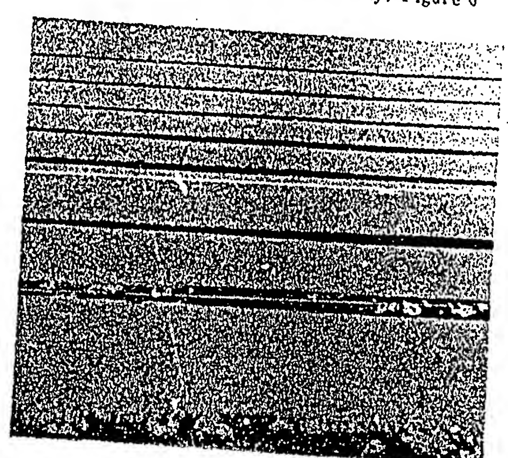


FIG. 6. Wires of varying size lying along a ⟨011⟩ stable direction after migration through 1 cm of silicon in the ⟨100⟩ direction. The stability of the wires increases with decreasing wire size.

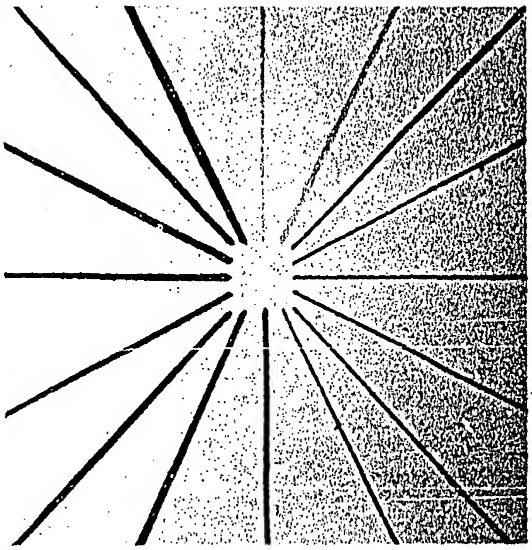


FIG. 7. A radial "sun" array of wires lying in a (111) plane after migration down a $\langle 111\rangle$ axis. All wire directions lying in the (111) plane are stable if the thermal gradient is aligned exactly along the $\langle 111\rangle$ direction.

shows wires along the $\langle 011\rangle$ direction with diameters ranging from 50 to 200 μ. After migration through 1 cm of silicon in the $\langle 100\rangle$ direction, only the fine wires below 100 μ in diameter were stable (Fig. 6). Thicker lines could be migrated [illegible] distances before they broke up.

In all experiments a critical factor influencing line stability was the parallelism of the applied thermal gradient to either the $\langle 100\rangle$, $\langle 110\rangle$, or $\langle 111\rangle$ crystallographic directions. An off-axis component of the thermal gradient decreases the stability of the migrating wire in all cases by causing toothlike facets to develop on the side faces of the wire.

2. $\langle 111\rangle$ axial wafers

The stability of wires lying in a (111) plane and migrating in a $\langle 111\rangle$ direction is not sensitive to the crystallographic direction of the wire as is shown by the "sun" pattern in Fig. 7. This general stability of wires lying in the (111) plane results from the fact that the (111) plane is the facet plane in the aluminum-rich liquid-silicon system [Fig. 5(c)].[13] Thus both the forward and rear faces of these wires are stable if the wire is not too thick.

On the other hand, the side faces of these wires lying in the (111) plane are not equally stable. Lines lying in the $\langle 1\bar{1}0\rangle$, $\langle 10\bar{1}\rangle$, and $\langle 01\bar{1}\rangle$ directions have (111)-type planes as side faces. These wires as a consequence are stable to any sideways drift that may be generated by any component of the thermal gradient not aligned exactly along the $\langle 111\rangle$ axis. Other wire directions in the (111) plane such as the $\langle 11\bar{2}\rangle$ lines develop ratchets on their side faces, if they drift sideways because of a slightly off-axis thermal gradient (Fig. 8) and may either eventually break or twist into a $\langle 1\bar{1}0\rangle$-type line direction (Fig. 9). Nevertheless, with a reasonably

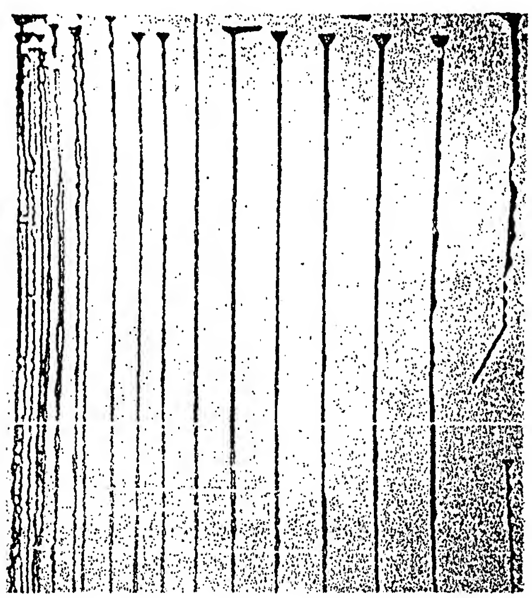


FIG. 8. An array of lines along the $\langle 11\bar{2}\rangle$ direction migrating down a $\langle 111\rangle$ axis. The thermal gradient is exactly aligned along the $\langle 111\rangle$ axis in the center of photograph but has sideways components directed towards the middle of the photograph at the right and left edges of the photo. These sideways thermal gradient components have caused sideways migration which in turn has induced serrations to develop on the outside edges of lines on the right-hand and left-hand side of the photo.

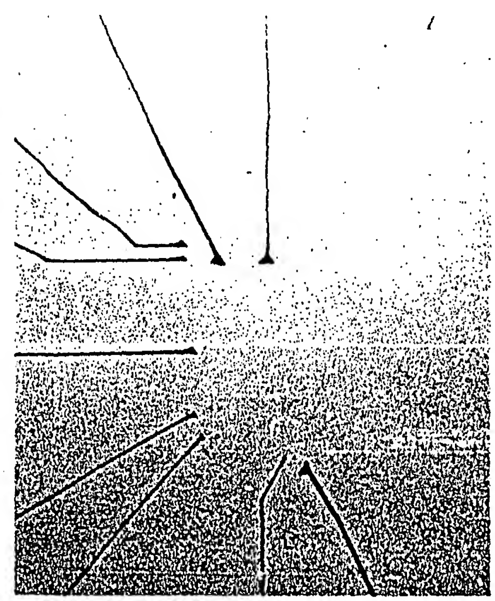
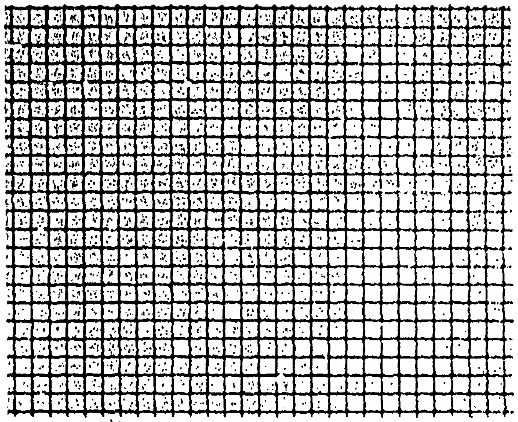
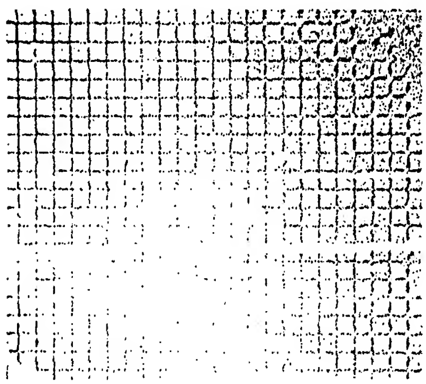


FIG. 9. A radial sun array of wires lying in a (111) plane after migration down a $\langle 111\rangle$ axis with a slightly off-axis thermal gradient. Some of the wires have partially twisted from $\langle 11\bar{2}\rangle$-type to $\langle 011\rangle$-type orientations.



(a)



(b)

FIG. 10. (a) A square grid of lines in the $\langle\bar{2}11\rangle$ and $\langle 0\bar{1}1\rangle$ directions after migration of 1 mm through silicon along a $\langle 111\rangle$ axis. (b) The variation in line thickness of the grid lines was caused by an uneven deposition of aluminum in the original etched line array.

TABLE I. The wafer plane, migration direction, stablewire directions, and stable wire sizes for the migration of aluminum-rich liquid wires through silicon. The stability of the migrating wire is sensitive to the alignment of the thermal gradient with the $\langle 100\rangle$, $\langle 110\rangle$, and $\langle 111\rangle$ axes, respectively. Group a is more stable than group b which is more stable than group c.

Wafer plane	Migration direction	Stable Wire directions	Stable Wire sizes (μ)
(100)	$\langle 100\rangle$	$\langle 011\rangle$	<100
		$\langle 0\bar{1}1\rangle$	<100
(110)	$\langle 110\rangle$	$\langle 1\bar{1}0\rangle$	<150
(111)	$\langle 111\rangle$	$\langle 01\bar{1}\rangle$	
		$\langle 10\bar{1}\rangle$ a	<500
		$\langle 1\bar{1}0\rangle$	
		$\langle 11\bar{2}\rangle$	
		$\langle 2\bar{1}\bar{1}\rangle$ b	<500
		$\langle 1\bar{2}1\rangle$	
		Any other direction c in {111} plane	<500

well-aligned thermal gradient, $\langle 11\bar{2}\rangle$-type wires can be migrated at least 1 cm through silicon without breakup or serrations. To demonstrate this flexibility in the $\langle 111\rangle$ migration direction, a square grid array with the wires aligned along $\langle\bar{2}11\rangle$ and $\langle 0\bar{1}1\rangle$ directions was successfully migrated through 1 cm of silicon[24] [Figs. 10(a) and 10(b)]. Both the initial grid geometry and dimensions have been preserved through the entire ingot. The initial deposited aluminum film was not uniform across the entrance face of the wafer with the result that a variation of thickness in the grid lines (1–4 mil) occurs across the sample. Note that the most uniform results are obtained with the finest-size grid wires.

To determine how fine the wire spacing can be made, a parallel array of lines aligned along a $\langle 0\bar{1}1\rangle$ direction with variable spacings was migrated down a $\langle 111\rangle$ axis through 1 cm of silicon. Lines spaced as close as 50 μ migrated uniformly without interfering with each other (Fig. 11). This minimum 50-μ spacing is currently limited by our masking and etching of 20-μ-deep line patterns.

Similar to the $\langle 100\rangle$ migration direction, the stability of wires migrating along the $\langle 111\rangle$ direction is a function of the wire diameter. Generally, the stability increases with decreasing wire diameter and wires less than 0.5 mm in diameter on the $\langle 111\rangle$ plane are stable in the 50 °C/cm gradients used in the current investigation.

3. $\langle 110\rangle$ axial ingots

Although no experiments were carried out on $\langle 110\rangle$ axial ingots, our results from the other ingots indicate that only wires with a $\langle\bar{1}10\rangle$ direction will be stable migrating down a $\langle 110\rangle$ axis in silicon [Fig. 4(b)]. The expected shape of such a stable wire is shown in Fig. 5(b).

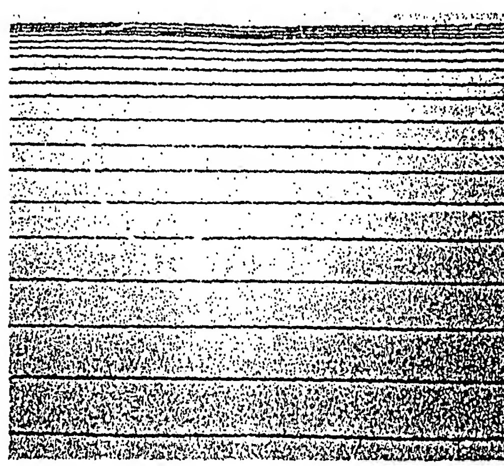


FIG. 11. A array of lines in the $\langle 0\bar{1}1\rangle$ direction with variable spacings after migration down the $\langle 111\rangle$ axis. The minimum spacing between lines of 50 μ is not limited by the thermomigration process but by our current etching and masking techniques.

III. SUMMARY

Table I and Figs. 4 and 5 summarize our observations of the wire directions, migration directions, wire shapes, and wire sizes that allow the stable migration of aluminum-rich liquid wires through bulk silicon. All of these results are consistent with the fact that the (111) plane is the solid-liquid interface facet plane in the aluminum-rich liquid-silicon system. An investigation of wire migration in the aluminum-rich liquid-germanium system was carried out by Wernick.[3] In his experiments, movements of wire zones across *surfaces* rather than through the bulk were observed for various surface planes and migration directions. Although the faceting plane is the same for this system [(111)], fewer stable migration directions were found presumably because of the constraints of surface migration in these experiments. In particular, the ⟨111⟩ migration direction in which wires in all directions lying in the (111) plane are stable was not observed. Since Si and Ge are very similar, it is anticipated that bulk experiments carried out in Ge would lead to very similar if not identical results to those found for silicon in the present investigation.

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